

# Orbitrap Mass Analyser: a Tool for Titan Complex Molecular Content Exploration

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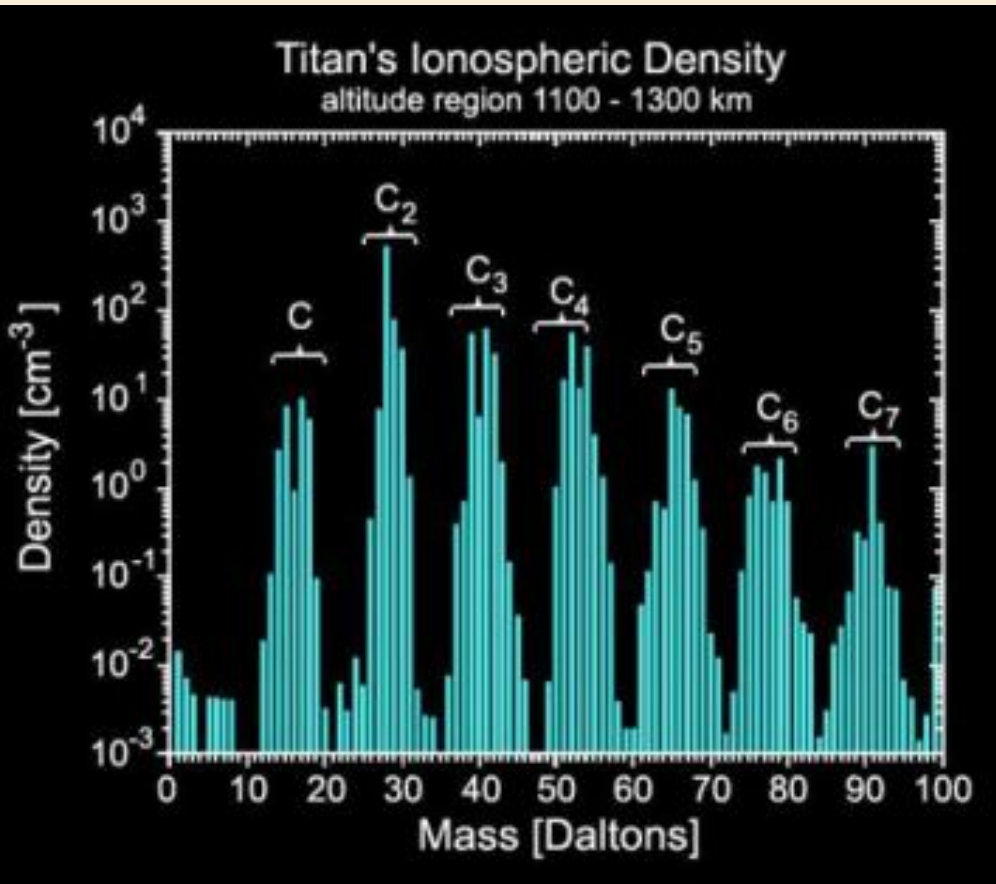
**Toulouse**  
**Paris**

High mass-resolution for Titan?



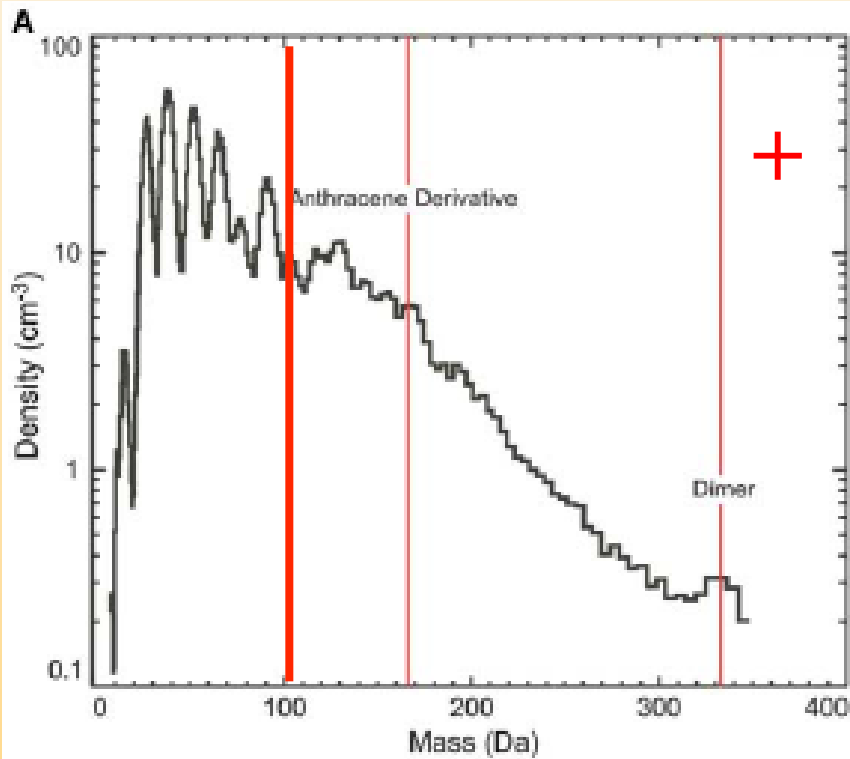
# Cassini (INMS)

## ionic densities in Titan ionosphere

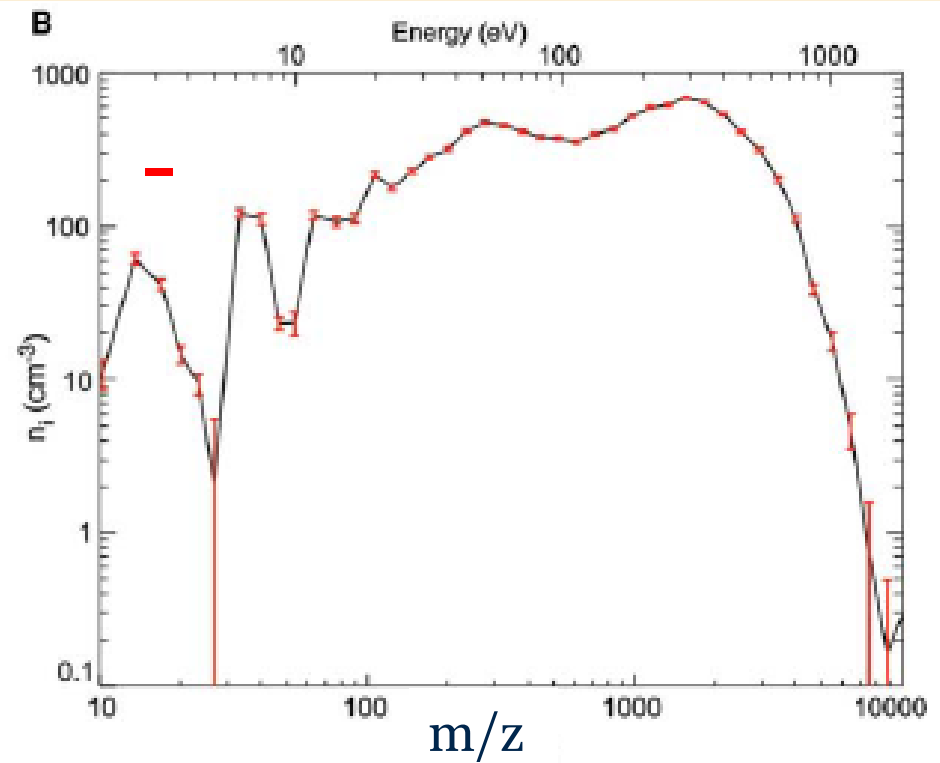


$C_7NH^+$	99.0109	resolution
$C_8H_3^+$	99.0235	7857
$C_4N_3H_9^+$	99.0797	1761
$C_5N_2H_{11}^+$	99.0923	7857
$C_6NH_{13}^+$	99.1049	7853
$C_7H_{15}^+$	99.1174	7920

# Big molecule synthesis ...



Positive ions  $< 350$



Negative ions  $> 1000$

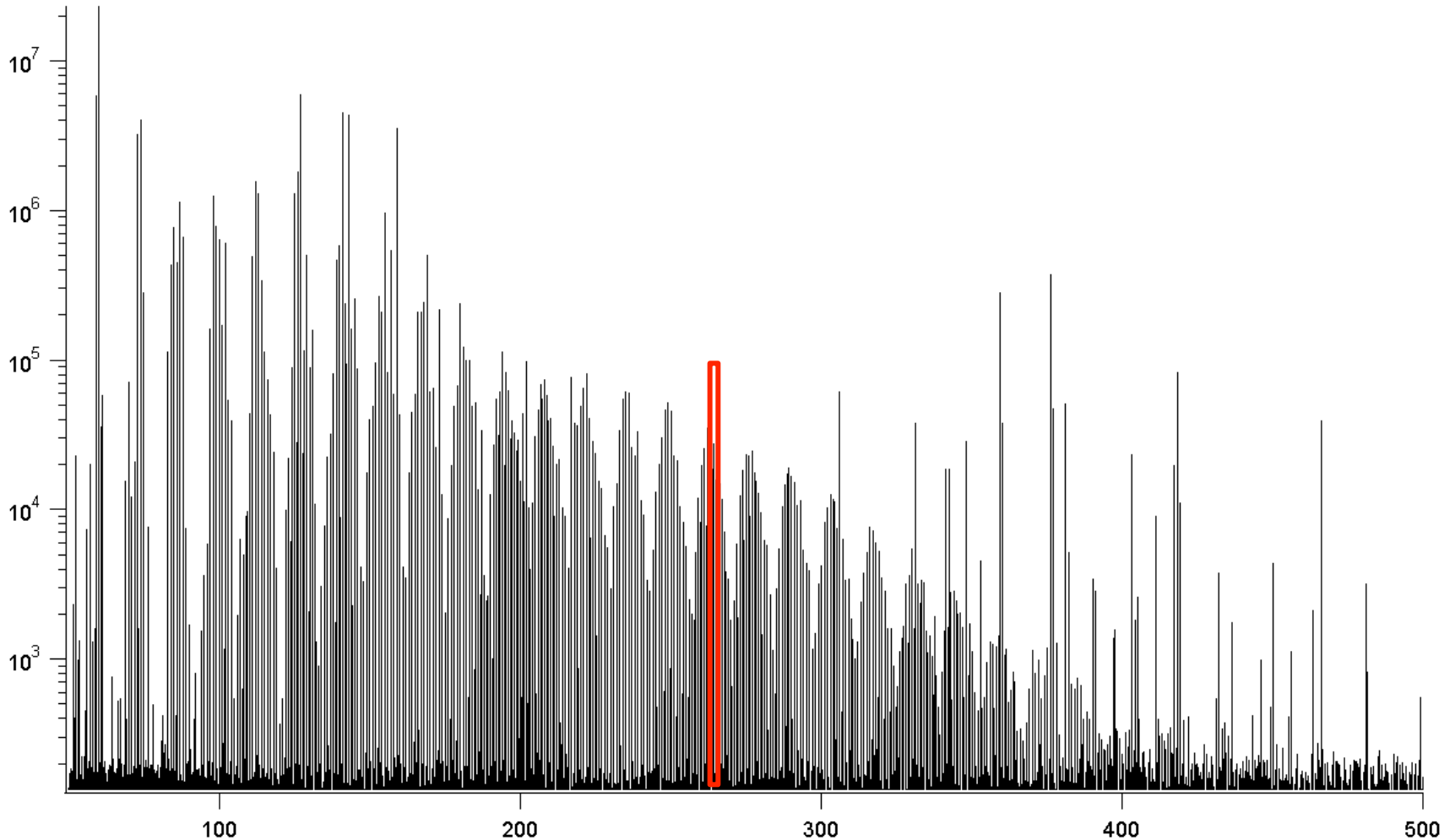
# Bio molecules synthesis...

## Formation of amino acids and nucleotide bases in a Titan atmosphere simulation experiment

				P2CO	P2COi	P5CO	P5COi	
				%N <sub>2</sub>	96.2	96.2	93.2	93.2
				%CH <sub>4</sub>	2	2	5	5
				%CO	1.8	1.8 C <sup>18</sup> O	1.8	1.8 C <sup>18</sup> O
Name	Mass	Formula	Fig					
Nucleotide Base								
cytosine	111	C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O	2	OT	OT	OT/GC-MS	OT	
uracil	112	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>		OT	OT	OT/GC-MS	OT	
thymine	126	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>		OT	OT	OT/GC-MS	OT	
adenine**	135	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	2	OT		OT/GC-MS		
guanine	151	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O		OT		OT/GC-MS		
Biological Amino Acid								
glycine	75	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>		OT		OT/GC-MS		
alanine	89	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>		OT		OT/GC-MS		
serine	105	C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>		OT		OT		
proline	115	C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>		OT		OT		
valine	117	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>		OT		OT		
threonine	119	C <sub>4</sub> H <sub>9</sub> NO <sub>3</sub>		OT				
isoleucine/ leucine	131	C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>		OT		OT		
asparagine	132	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>		OT		OT		
glutamine	146	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>		OT		OT		
lysine	146	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>		OT		OT		
histidine	155	C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>	2	OT		OT	OT	
phenylalanine	165	C <sub>9</sub> H <sub>11</sub> NO <sub>2</sub>		OT		OT		
arginine	174	C <sub>6</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>		OT		OT		

Horst et al. Accepted in Astrobiology

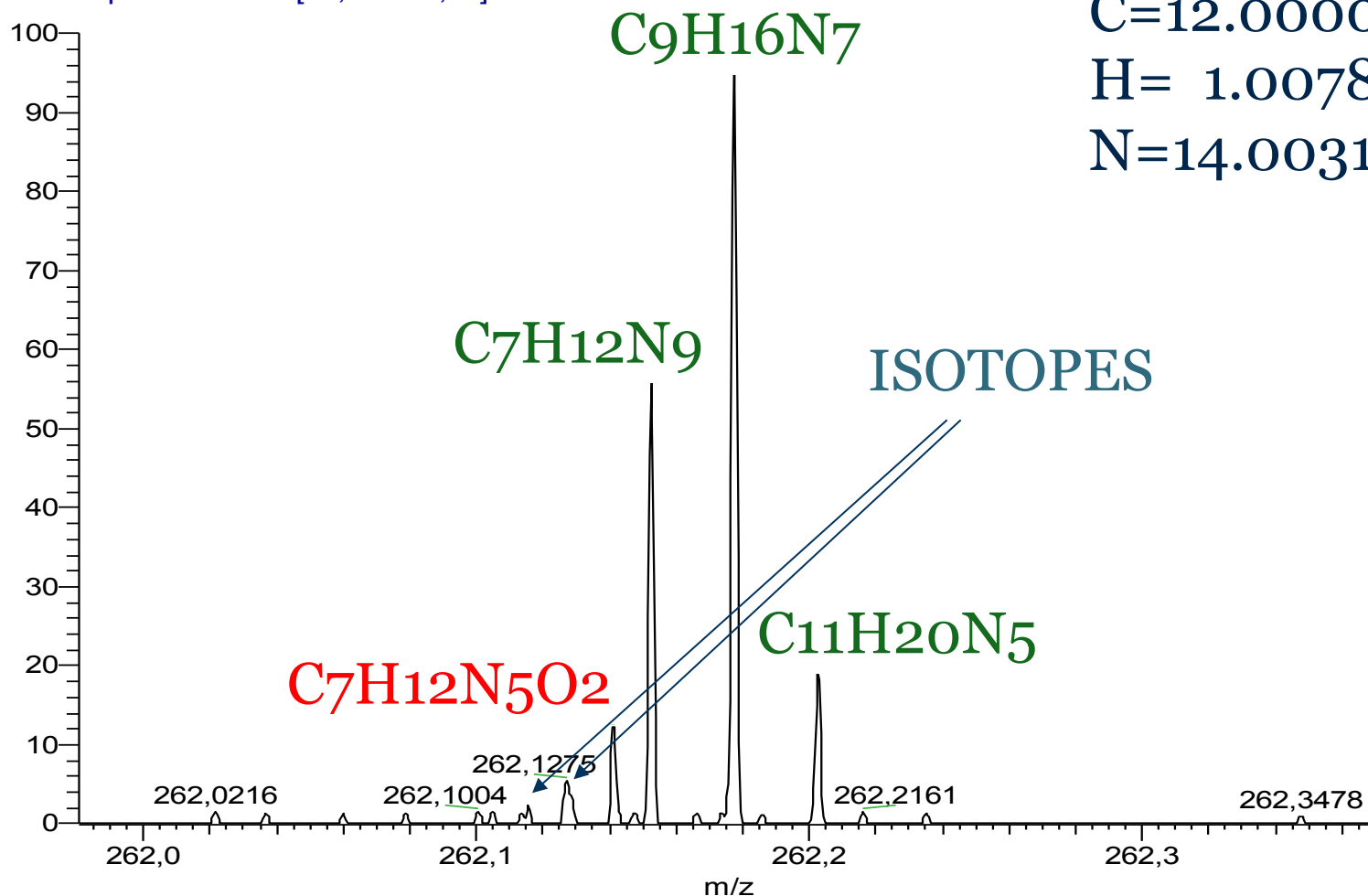
# Tholins mass spectrum at high resolution



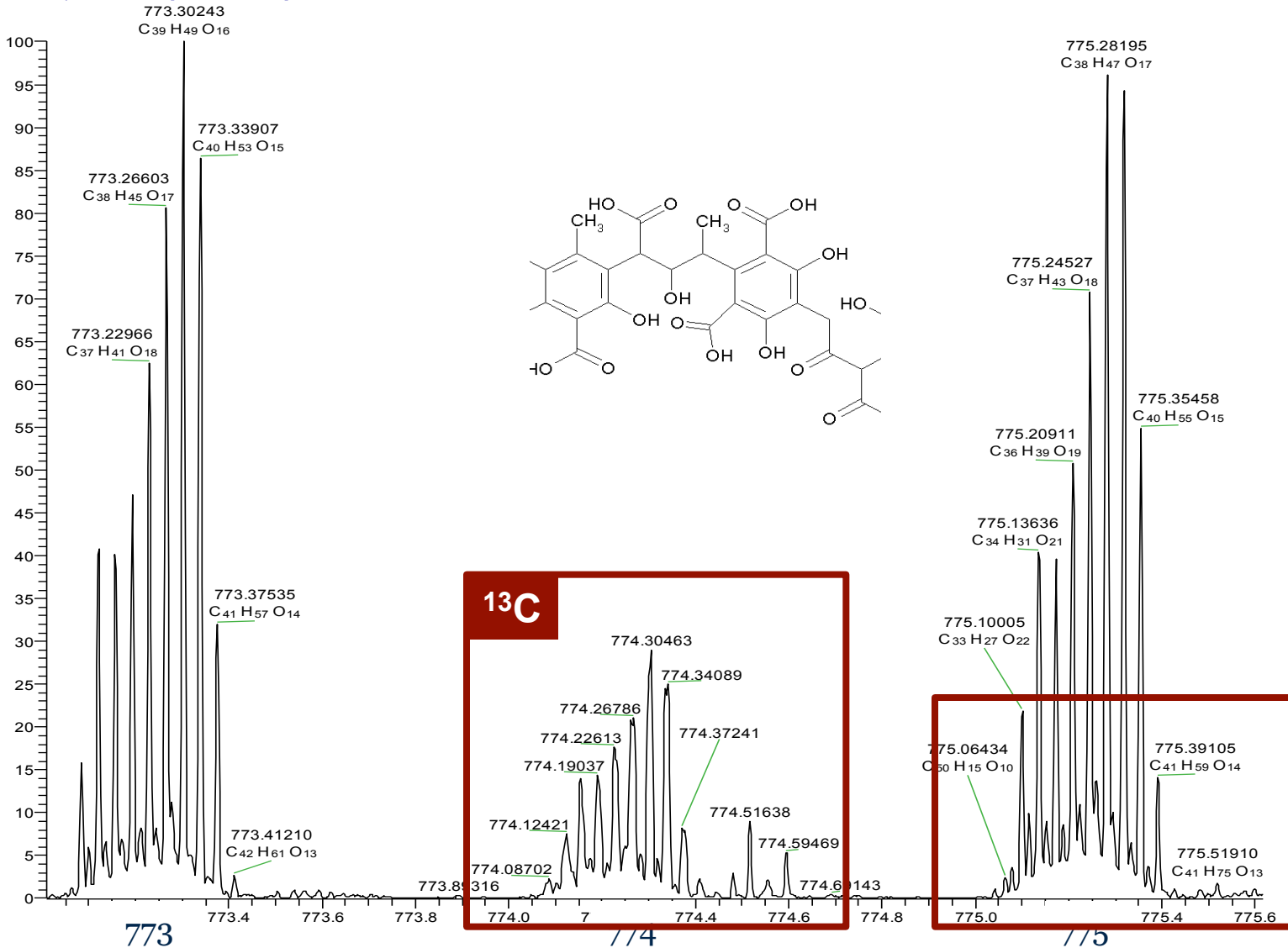
# Zoom on mass 262

070511\_Lot1MeOH\_b #663-697 RT: 19,32-20,28 Av. 55 NL: 1,02E5  
T: FTMS + p ESI Full ms [50,00-500,00]

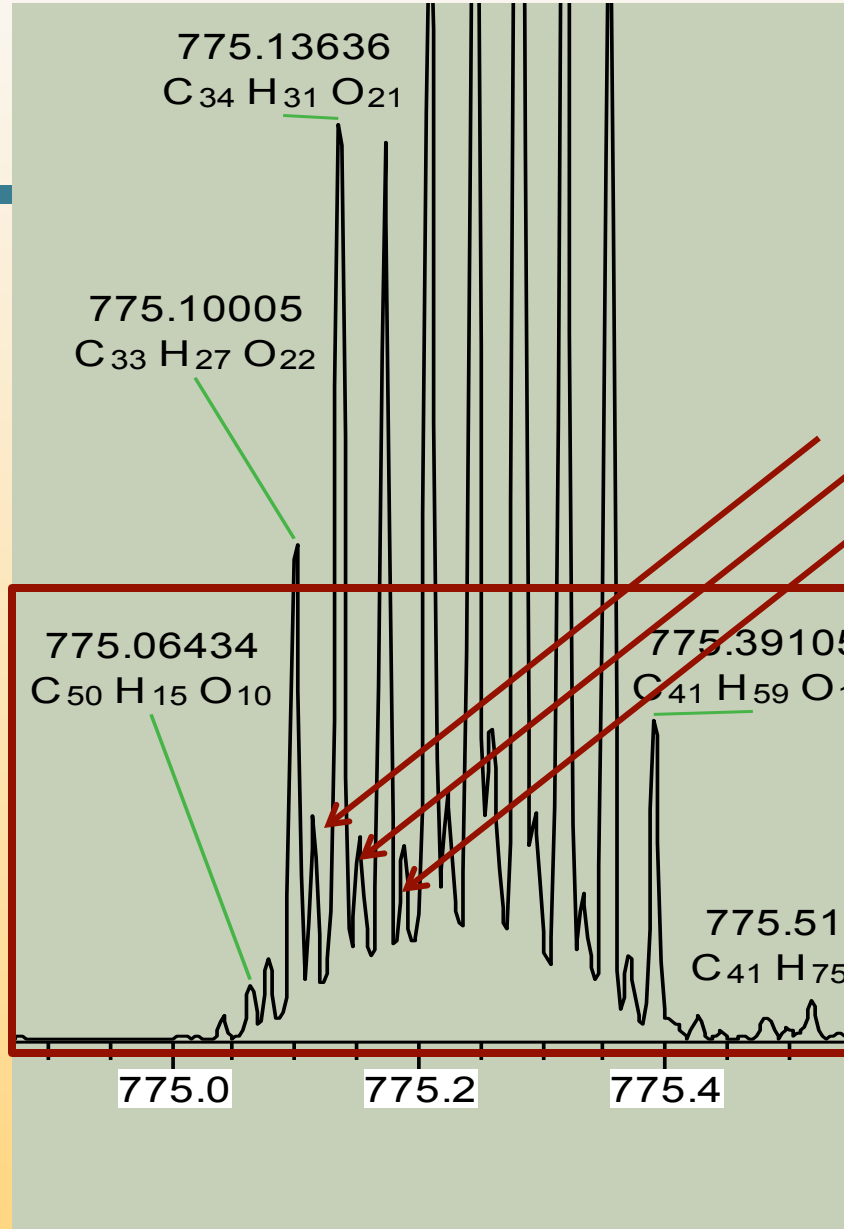
C=12.0000  
H= 1.0078  
N=14.0031



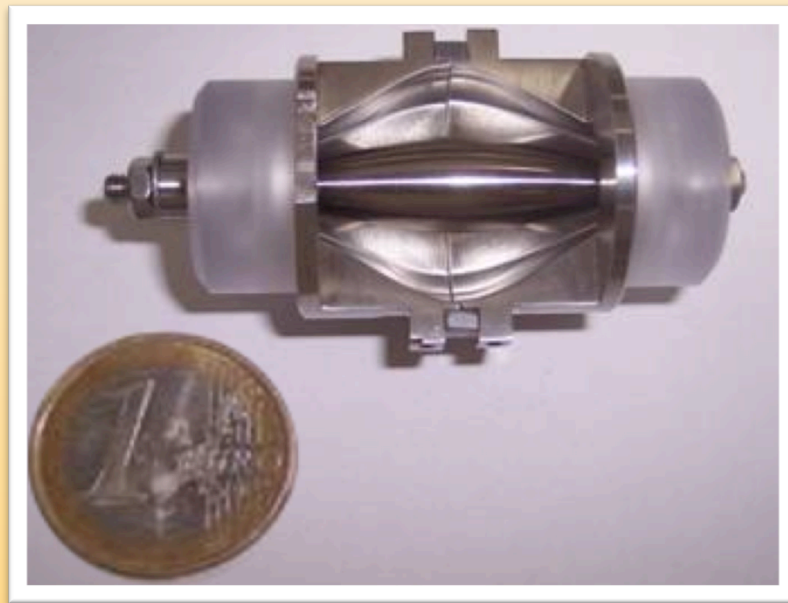
# Isotopical abundancies, example on complex mixture...





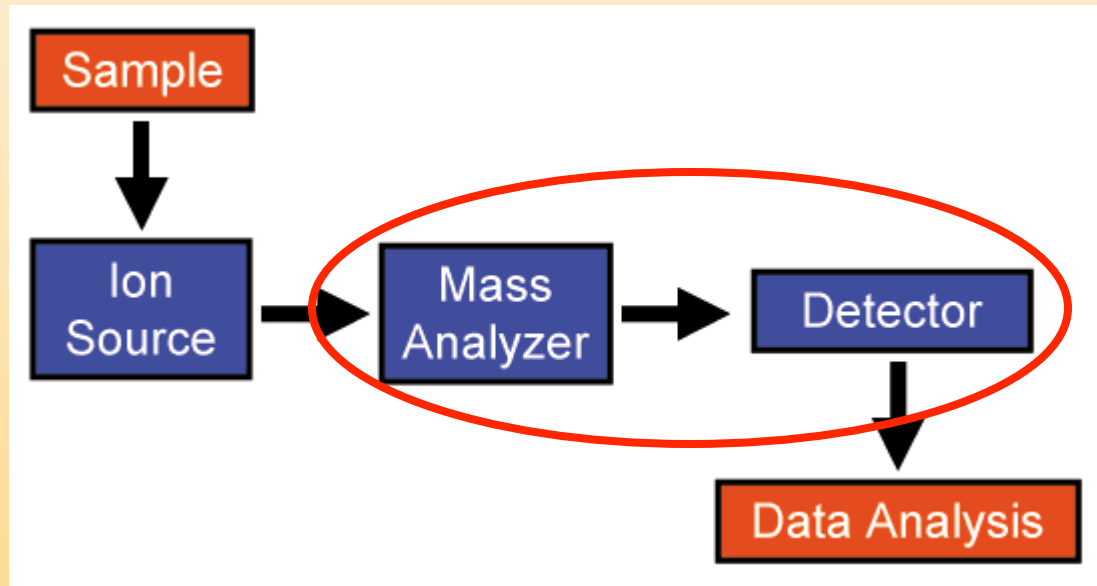


# Orbitrap mass Analyser ?

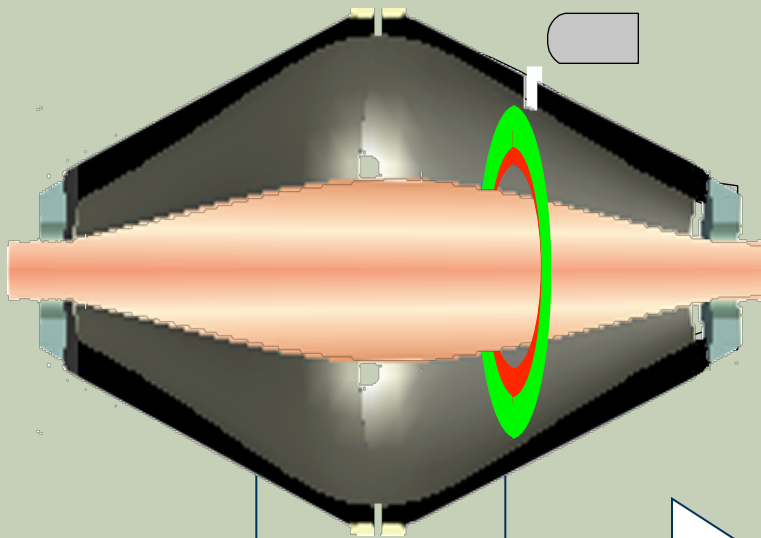


# Preliminary remark, what is orbitrap...

## Mass Spectrometry :

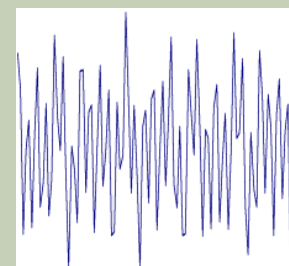


# Perfect quadro logarithmic potential



$$\omega = \sqrt{\frac{k}{m/z}}$$

record movement of  
unperturbed ions during  
>500ms  
pressure  $<10^{-9}$  mbar!

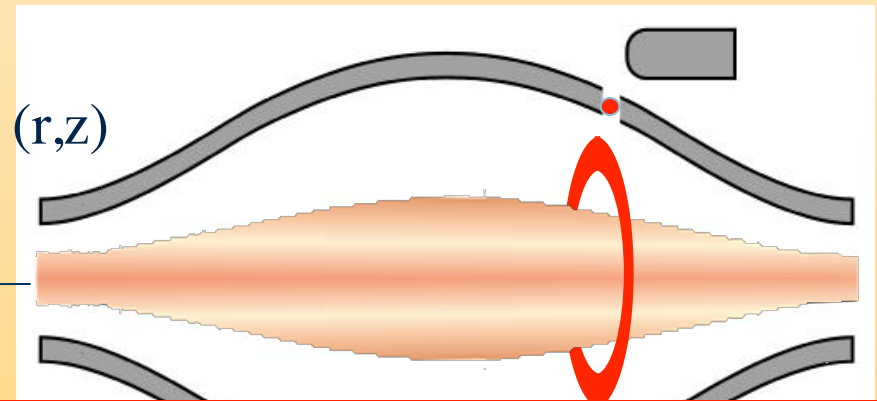
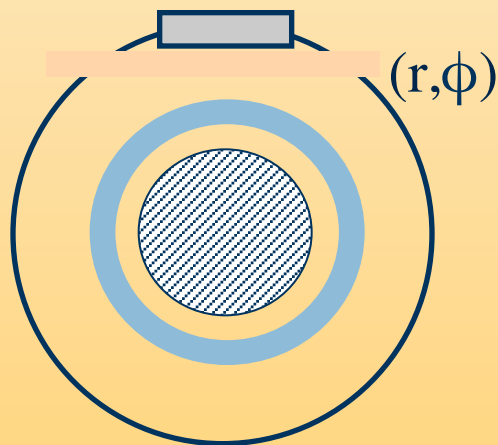


# How to inject and stabilize ions in this perfect potential? “Electrodynamic squeezing”

- a bunch of ions enters in the field, tangentially
- ions are squeezed towards central electrode by variation of its potential (deepening of well)
- The excitation of quadratic movement is inherent to “off axis” injection



Need to pulse ions in the trap!



Need for very stable HV potential  
During measurement!

# Orbitrap, potential

- Ultra high resolution: 100 000 at mass 400, adjustable during mission, as it depends only on the integration time
- Very small volume, lightweight :  $l=4$  ,  $f= 4$  cm
- Good detection Dynamic : 50 000 per spectrum
- Positive or negative Ions as only one potential to invert
- All ions are analysed simultaneously
- No detector, no saturation, ...
- no RF, no moving part
- Ideal for solids or aerosols

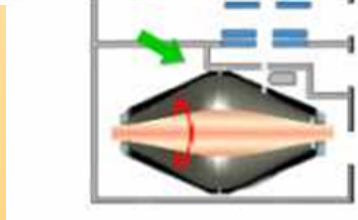
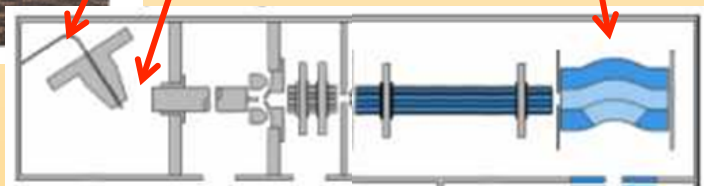
# Orbitrap for Titan



Sample handling

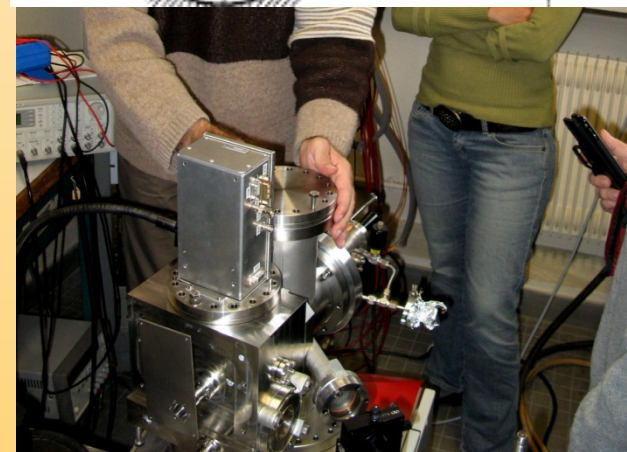
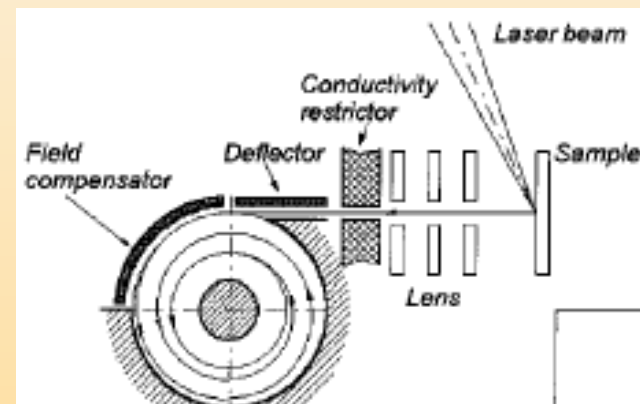
ionization

Ion accumulation

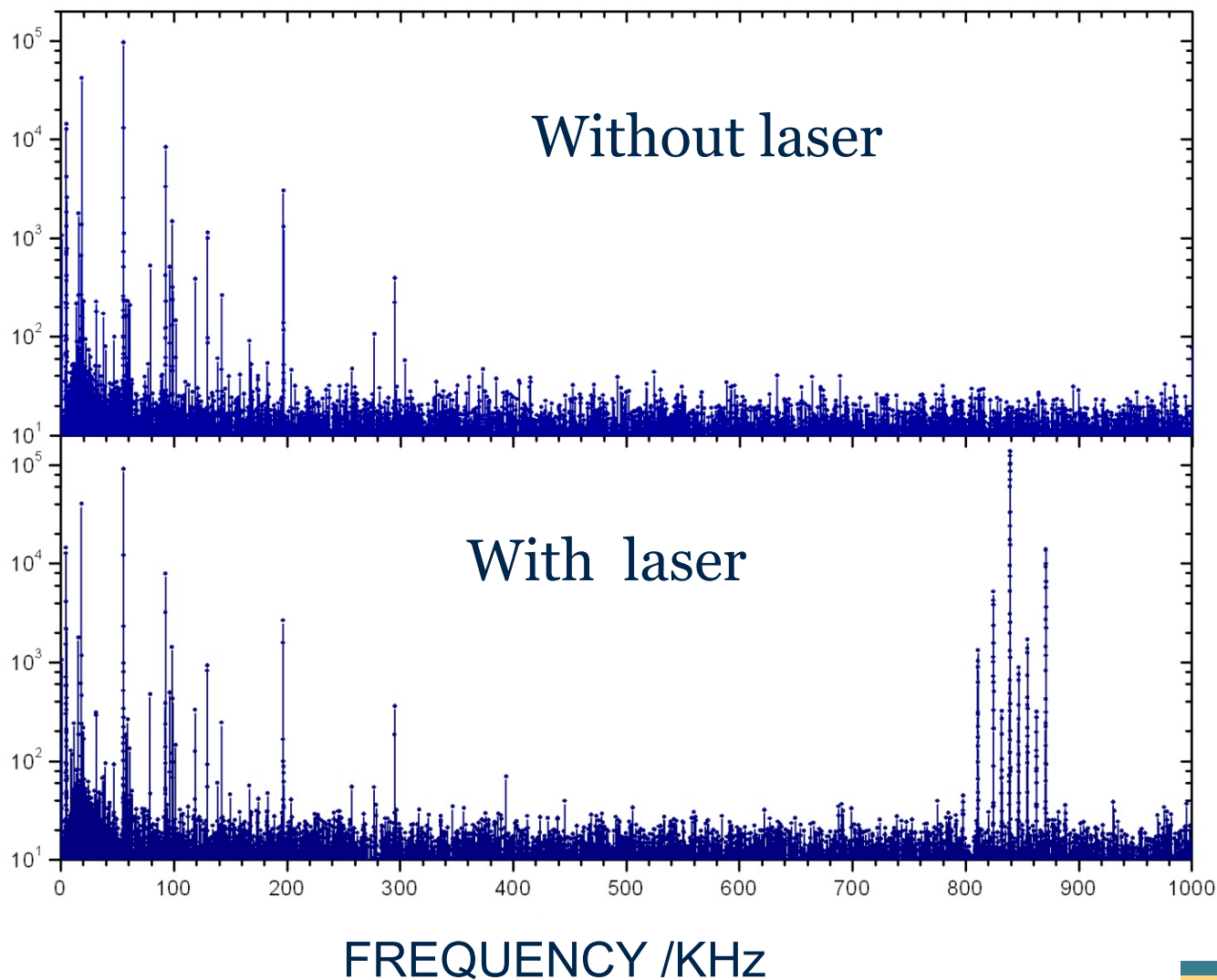


Study of optimized  
MS instrument for the analysis of  
aerosols/solids/liquids present in  
the deep atmosphere/surface of  
Titan

## Orbitrap prototype in Orléans



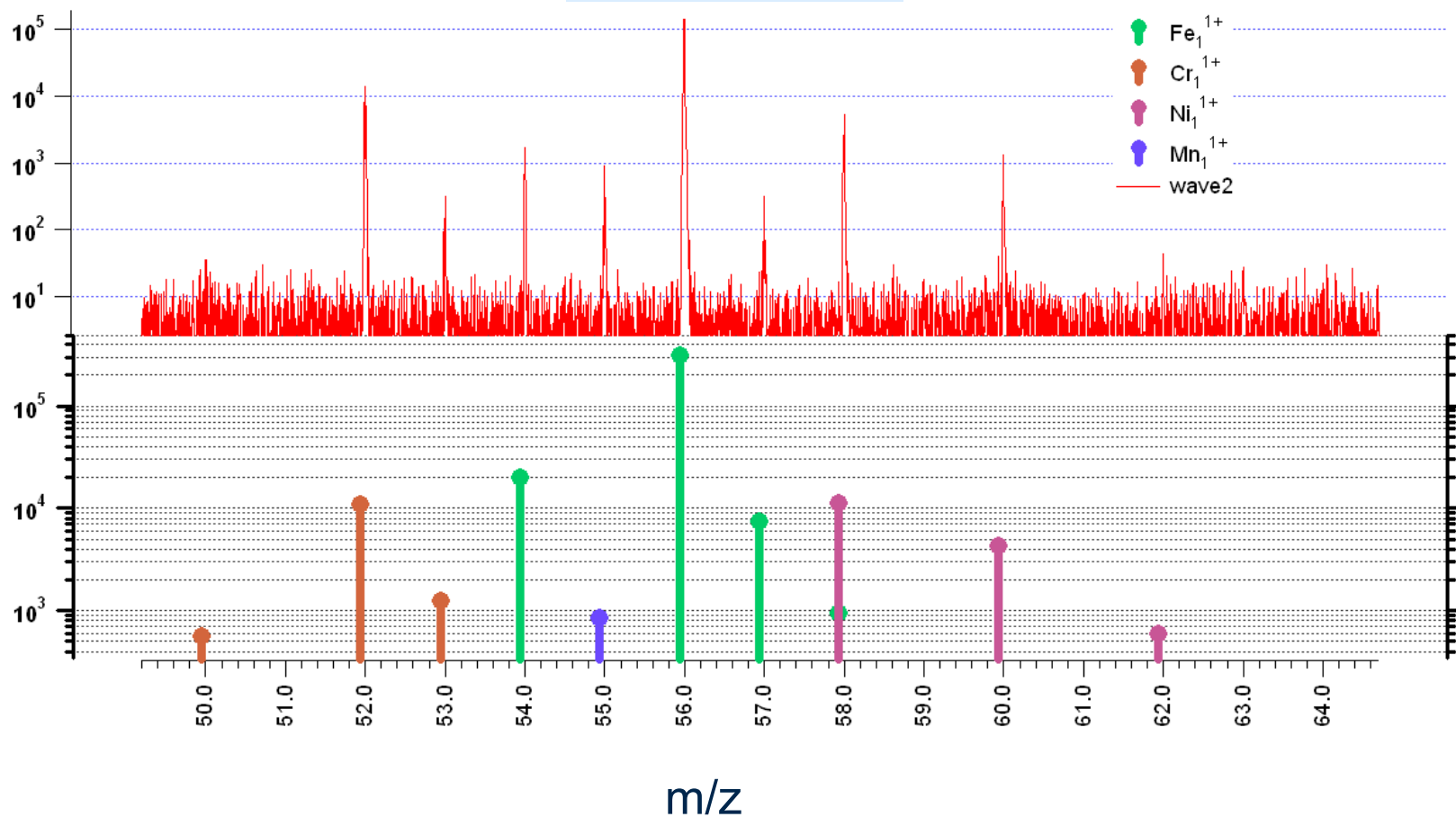
# Performances of prototype...



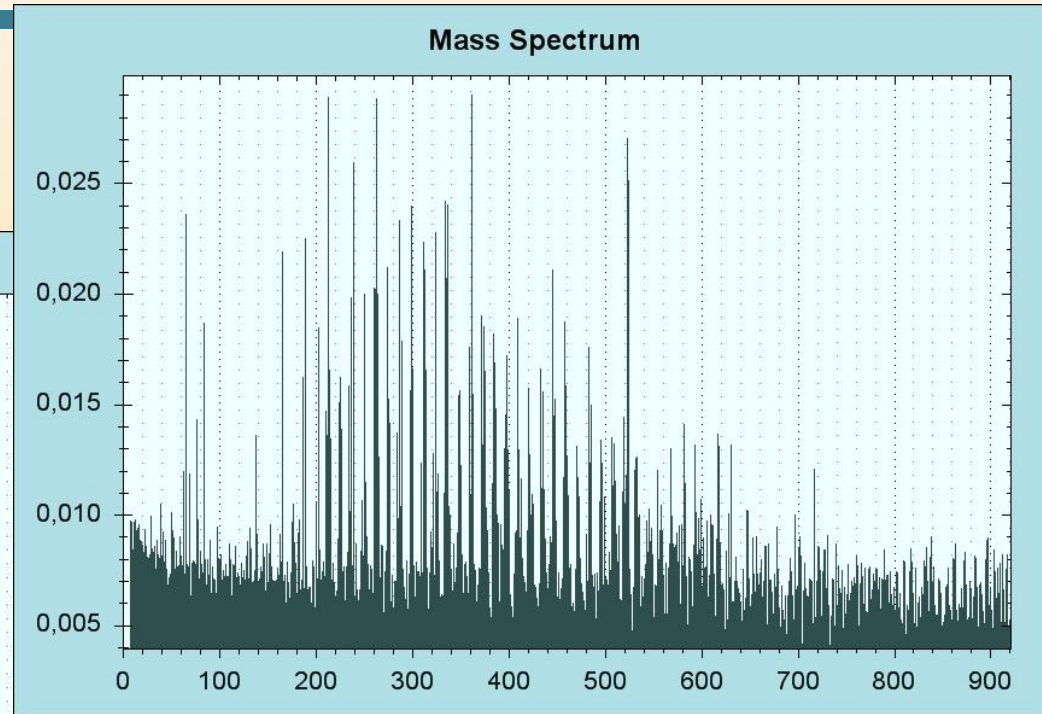
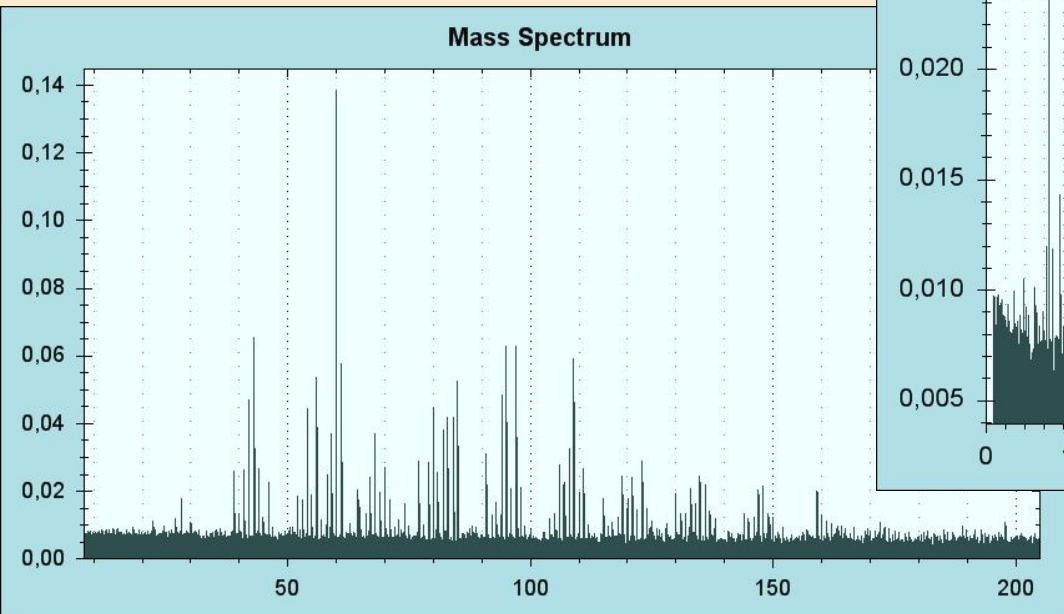


# 1 laser shot on Stainless steel

R=280 000



# Tholins survive the laser desorption/ionization



# Conclusions

- # Going back to Titan, we need to do much better than Cassini.
- # We know that very large (bio)organic molecules are produced/  
present in
  - Atmosphere                    **Aerosols**
  - Surface                        **Liquids / solids**
- # Request for very high resolution mass spectrometry to be characterized.
- # Orbitrap is a very promising analyser/detector for this purpose.
- # However big challenges remain:
  - Sample handling ?
  - Ionization method ?
  - High-Vacuum generation/maintenance ?
  - Beyond formulas, what about structural analysis ?
  - ...
- # Further info ? Come & visit posters **7A/B**  
**Briois, Cornelli and Thirkell**